

SOME PROBLEMS IN THE MODELING OF COMPLEX CHEMICAL PROCESSES

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INTRODUCTION

In the last decade, the "mature" science of chemical kinetics has entered what may be termed the "Computer Age". Thirty years ago, the goal of chemical engineers working with a chemical process would be to obtain an explicit rate expression describing the rate dependence on experimental parameters. For diverse reasons, this is no longer a sufficient result. The availability of high speed computers together with relevant kinetic and thermochemical data have today made possible the description of a complex chemical process in terms of the elementary kinetic steps comprising it. Explicitness is no longer necessary

This evolution has been accelerated by a need to satisfy increasingly stringent environmental requirements as well as the need to reduce the cost of optimization of chemical processes. Experiments, particularly in larger scale equipment can become prohibitively expensive and time consuming. Computer experiments, on the contrary are inexpensive and can be adapted, in combination with the appropriate fluid mechanics, to rapid and inexpensive scaling. Laboratory experiments in 1 cm diameter tubing are relatively cheap and easy to do but may not represent the results of an industrial flow process carried out in 10 cm to 20 cm pipes.

Fuel chemistry has been one of the pioneers in adapting computer kinetics to its various needs. In doing so it has brought together the chemical engineer, the academic kineticist and the fluid dynamicist in what is truly today, a multi-disciplinary effort. Despite the considerable reluctance of each of these specialists to interact with each other, there is no alternative to a directed and active dialogue. This "social" barrier has been little discussed but has been as much a challenge as the technical problems themselves. From my own experience as an academic kineticist who has done much industrial consulting, I would estimate that the usual mode of arms length interaction between kineticist and engineers has generated a 10 to 20 year lag in the utilization of basic science. A good part of this lag arises from difficulties in the basic kinetic science itself and this is the subject I would like to discuss here.

Kinetic modeling of a complex chemical process requires the following:

- 1.) A complete knowledge of the elementary kinetic steps--the mechanism.
- 2.) Accurate thermochemical data on all of the species involved.
- 3.) Accurate kinetic data for each step.
- 4.) An understanding of surface processes which may be of importance.

Historically, the first attempt to model a complex system was the Rice-Herzfeld analysis of the thermal cracking of hydrocarbons almost 60 years ago.¹ While enormously simplified compared to our current understanding this work provided the prototype for all subsequent efforts. The problems, then as now remain the same, namely, the four requirements outlined above.

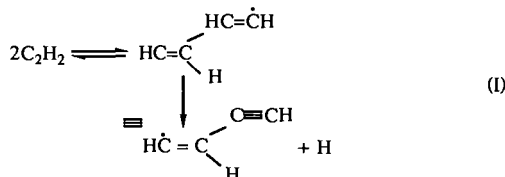
Mechanism

It is impossible to prove that any given mechanism is correct or complete. Its operational test is that it reproduces quantitatively all available data on any chemical process. An interesting example is provided by the pyrolysis of acetylene. While early work on acetylene had been interpreted in terms of a free radical mechanism² recent workers have tried to interpret this chemistry in terms of an active carbene isomer of acetylene, vinylidene:^{3,4}

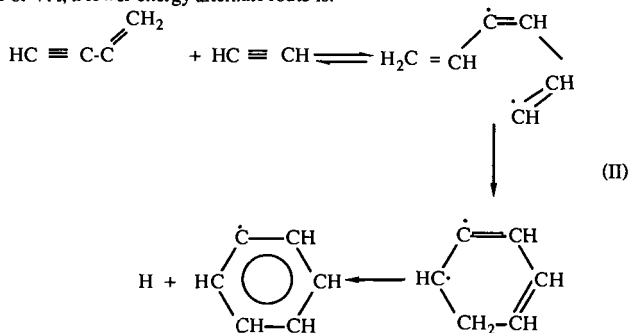


The reason for invoking such a species was that the conventional free radical mechanism could not account for the observed rate of pyrolysis of acetylene by as much as a factor of 100 at 1000°K. However, a recently proposed mechanism invoking a different radical initiation process has been shown to account for all the features of C_2H_2 pyrolysis.⁵

This most recent free radical mechanism makes use of vinyl acetylene (VA), the first product of acetylene pyrolysis, as an autocatalytic agent which provides a fast low energy path to free radical initiation. In the absence of VA free radicals are provided by a bimolecular process:



In the presence of VA, a lower energy alternate route is:



This second path (II) has an activation energy of 30 kcal whereas the first path (I) has $E = 67$ kcal. Using estimated rate constants consistent with the data on VA-acetylene copyrolysis⁶ it turns out that at a $[\text{VA}]/[\text{C}_2\text{H}_2]$ ratio of 10^{-7} at 800°K the two paths are equal in rate. The well documented induction period in acetylene pyrolysis is then the time required via slow initiation path (I) to produce the small amounts of VA needed to permit path (II) to take over as the initiation source.



Surface Processes

Surface chemistry still represents the very gray area of modeling. We have very little detailed knowledge of the thermochemistry or kinetics of surface reactions. Anyone who has worked with high temperature pyrolysis reactions is familiar with "coking" in hydrocarbon systems and the importance of surface generated reactions. In the past two years the discovery of important reactions on the surfaces of nitric acid ice crystals in the Antarctic stratosphere has provided an unexpected jolt to the atmospheric kineticists. Recent work on diamond formation from CH_4 at high temperature has given an enormous stimulus to the study and understanding of radical reactions of surfaces.¹⁰ Hopefully, this will produce some quantitative kinetic and thermochemical data from which we can build a systematic base. For the moment, surface reactions will continue to be treated empirically.

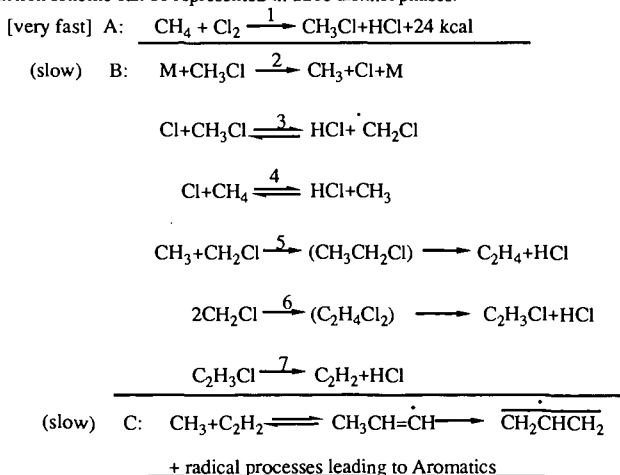
It is well however to note that for radical-molecule reactions at surfaces, these are essentially members of the gas phase family subject only to non-bonded interactions due to steric crowding.

Metals and metal oxides may differ basically from hydrocarbon surfaces in that they present very polar environments and their reactions may resemble ionic or ion-pair reactions rather than the mildly polar reactions of hydrocarbons and their radicals.

Equally of note is the fact that there is a large loss in entropy for a gas phase species on chemisorbing at a surface site. We can estimate entropies of chemisorbed species to an accuracy of about 1-2 cal/mole $^\circ\text{K}$ so that with a knowledge of the surface concentration we can estimate heats of chemisorption to 1 kcal.

The High Temperature Reaction of $\text{Cl}_2 + \text{CH}_4$

A recent example of modeling with importance in C-I chemistry has just been done in my laboratories at USC.¹¹ We have modeled the reactions of $\text{Cl}_2 + \text{CH}_4$ mixed hot at 700 to 900 $^\circ\text{K}$. It is an extremely rapid, exothermic reaction capable of reaching peak temperatures of 1400-1500 $^\circ\text{K}$. The reaction scheme can be represented in three distinct phases:



Modeling has shown that the gas phase reaction will produce up to 70 and 80% of useful products per mole Cl_2 with about 78% conversion of CH_4 per pass. Useful products are predominantly $\text{C}_2\text{H}_2 + \text{C}_6\text{H}_6$ with lesser amounts of ethylene, butadiene, vinyl chloride, and styrene. Only trace amounts of naphthalene or higher species are formed.

Comparison with laboratory data in high surface reactors suggest that only surface reactions can account for the carbon formation observed at longer residence times. This system which represents an economically attractive methane convertor presents some very interesting engineering problems; rapid mixing of hypergolic species, hot $\text{Cl}_2 + \text{CH}_4$ and rapid quenching (100 msec) of the reaction stream before significant surface reactions have occurred.

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